EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF AROCLORS

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Exhibit D - Analytical Methods for Aroclors

Table of Contents

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1.0 SCOPE AND APPLICATION

1.1 In 1978, US Environmental Protection Agency (USEPA) Headquarters and Regional representatives designed analytical methods for the analysis of chlorinated pesticides and Aroclors in hazardous waste samples. These methods were based on USEPA Method 608, Organochlorine Pesticides, and Polychlorinated Biphenyls (PCBs). In 1980, these methods were adopted for use in the Contract Laboratory Program (CLP). As the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evolved, the CLP methods, as well as their precedent USEPA 600 Series methods, established the basis of other USEPA methods to perform the analysis of Aroclors contained in hazardous waste samples (i.e., SW-846). The following CLP method has continuously improved to incorporate technological advancements promulgated by USEPA, and has continued to set the standard for the preparation, extraction, isolation, identification, and reporting of Aroclors [and pesticides in Exhibit D (Analytical Method for the Analysis of Pesticides)] at hazardous waste sites.

1.2 The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites to determine the presence and concentration of the Aroclors found in the Target Compound List (TCL) in Exhibit C (Aroclors). The method can be used for determining analyte concentrations in the range from the Contract Required Quantitation Limits (CRQLs) to one million times the CRQL in these matrices when appropriate dilutions are made. The method includes sample extraction, extract cleanup techniques, and Gas Chromatograph/Electron Capture Detector (GC/ECD) analytical methods for Aroclors.

2.0 SUMMARY OF METHOD

2.1 Water

Continuous liquid-liquid extraction (CLLE) or separatory funnel extraction (SFE) procedures are employed for aqueous samples. A 1 L volume of sample is spiked with the surrogate solution and extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried with anhydrous sodium sulfate, concentrated, and cleaned up by Gel Permeation Chromatography (GPC) (GPC cleanup is optional). The extract is then solvent exchanged into hexane, subjected to a sulfuric acid cleanup, and the final volume adjusted to 1 mL or 2 mL. The extract is analyzed using a dual column wide-bore capillary Gas Chromatograph/Electron Capture Detector (GC/ECD) technique.

2.2 Soil/Sediment

A 30 g aliquot of sample is spiked with the surrogate and then mixed with anhydrous sodium sulfate and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture by sonication, Soxhlet extraction, or pressurized fluid extraction. The extract is filtered, concentrated, and cleaned up by GPC (GPC cleanup is optional). The extract is then solvent exchanged into hexane, subjected to a sulfuric acid cleanup, and the final volume adjusted to 1 mL or 2 mL. The extract is analyzed using a dual column wide-bore capillary GC/ECD technique.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in gas chromatograms. These materials must be routinely demonstrated to be free from interferences under the sample preparation and analysis conditions by analyzing method blanks. Interferences caused by phthalate esters can pose a major problem in Aroclor analysis. Because common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix Interferences

Matrix Interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures must be used to remove such interferences in order to achieve the Contract Required Quantitation Limits (CRQLs).

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in the chemical analyses.

Specifically, concentrated sulfuric acid and the 10 N sodium hydroxide solution are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 Aroclors covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor must document any use of alternative equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors

Equipped with polytetrafluoroethylene (PTFE) or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.1.2 Separatory Funnels - 2 L with PTFE stopcock.

6.1.3 Ultrasonic Preparation - A horn-type device equipped with a titanium tip, or a device that will give the equivalent performance.

6.1.3.1 Ultrasonic Cell Disruptor - Minimum power output of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disruptor for extraction of samples with low and medium/high concentration.

6.1.3.2 Use a 1/4 inch horn for the low concentration method and a 1/8 inch tapered microtip attached to a 1/2 inch horn for the medium/high concentration method.

6.1.4 [Automated] Soxhlet Extraction System - With temperature-controlled oil bath. Tecator bath oil should be used with the Soxhlet extractor (Silicone oil may not be used because it destroys the rubber parts). Accessories and consumables for the automated Soxhlet system include:

6.1.4.1 Cellulose Extraction Thimbles - 26 mm ID x 60 mm, contamination free.

6.1.4.2 Glass Extraction Cups (80 mL) (set of six required for the HT-6).

6.1.4.3 Thimble Adapters (set of six required for the HT-6).

6.1.4.4 Viton Seals.

6.1.5 Pressurized Fluid Extraction Device.

6.1.5.1 Dionex Accelerated Solvent Extractor or Supelco SFE-400 with appropriately sized extraction cells. Currently, cells are available that will accommodate 10 g, 20 g, and 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure requirements (2000+ psi) necessary for this procedure.

6.1.5.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.1.6 Drying Column - 20 mm ID borosilicate chromatographic column with borosilicate glass wool at bottom and a PTFE stopcock.

6.1.7 Syringes - 5 mL, 100 µL, and 1000 µL.

6.1.8 Vials - 1, 2, 10, 40, 60 mL glass with PTFE-lined screw-caps or crimp tops.

6.1.9 Disposable Glass Pasteur Pipet and Bulb - 1 mL.

6.1.10 Graduated Cylinder - 1 L capacity, 100 mL.

6.1.11 Erlenmeyer Flask - 250 mL.

6.1.12 Graduated, Conical-Bottom Glass Tubes - 15 mL or 10 mL Kuderna-Danish (K-D) concentrator tube.

6.1.13 Beakers - 400 mL.

6.1.14 Volumetric Flasks - 10 mL to 1000 mL.

6.2 Kuderna-Danish (K-D) Apparatus

6.2.1 Concentrator Tubes - 10 mL, graduated.

6.2.2 Evaporation Flasks - 500 mL.

6.2.3 Snyder Column - Three-ball macro.

6.2.4 Snyder Column - Two-ball micro.

6.2.5 Springs - ½ inch.

6.3 pH Indicator Paper - pH range including the desired extraction pH.

6.4 Boiling Chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide, or equivalent).

6.5 Solvent Vapor Recovery System.

6.6 Water Bath - Heated, with concentric ring cover, capable of temperature control (±5°C).

NOTE: The water bath should be used in a hood.

6.7 Heating Mantle - Rheostat controlled.

6.8 Apparatus for Determining Percent Dry Weight.

6.8.1 Drying Oven - Capable of maintaining 105°C.

6.8.2 Desiccator.

6.8.3 Crucibles - Porcelain or disposable aluminum.

6.9 Apparatus for Grinding - Capable of reducing particle size to less than 1 mm.

6.10 Analytical Balance - Capable of weighing to 0.001/0.0001 g. The balances must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balances must be

calibrated with Class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

6.11 Aluminum Weighing Dish.

6.12 pH Meter - With a combination glass electrode. Calibrate according to the manufacturer's instructions. The pH meter must be calibrated prior to each use.

6.13 Vacuum or Pressure Filtration Apparatus.

6.13.1 Buchner Funnel.

6.13.2 Filter Paper - Whatman No. 41, or equivalent.

6.14 Sonabox - Recommended with ultrasonic disruptor for decreasing cavitation sound.

6.15 Glass Scintillation Vials - 20 mL, with PTFE-lined screw-caps.

6.16 Spatula - Stainless steel or PTFE.

6.17 Filter Disk - 1.91 cm, Type D28 (Whatman 10289356, or equivalent).

6.18 Cell Cap Sealing Disk (Dionex 49454, 49455, or equivalent).

6.19 Gel Permeation Chromatography (GPC) Cleanup System

6.19.1 GPC System - Systems that perform satisfactorily have been assembled from the following components: an HPLC pump; an auto sampler or a valving system with sample loops; and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Section 10.3.1.

6.19.1.1 Chromatographic Column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached so that the column exit flow can be shunted either to the UV flow-through cell or the GPC collection device.

6.19.1.2 Guard Column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319, or equivalent).

6.19.1.3 Bio Beads (SX-3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.19.1.4 UV Detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.19.1.5 Strip Chart Recorder - Recording integrator or laboratory data system.

6.19.1.6 Syringe Filter Assembly, disposable, 5 micron.

NOTE: Some instrument manufacturers recommend a smaller micron filter disc. Consult your instrument operation manual to determine the proper size filter disc to use in your system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

6.20 Sulfuric Acid Cleanup System

6.20.1 Syringe or Class A volumetric glass pipet; 1.0, 2.0, and 5.0 mL.

6.20.2 Vials - 1, 2, and 10 mL, glass with PTFE-lined screw-caps or crimp tops.

6.20.3 Vortex Mixer.

6.21 Gas Chromatograph (GC)

6.21.1 The GC must adequately regulate temperature in order to give a reproducible temperature program and have a flow controller that maintains a constant column flow rate throughout temperature program operations. The system must have all required accessories including syringes, analytical columns, and gases.

6.21.2 GC Columns - Two wide-bore (0.53 mm ID) fused silica GC columns are required. A separate detector is required for each column. The specified analytical columns are:

6.21.2.1 30 m x 0.53 mm ID, 0.5 µm or 0.83 µm film thickness, DB-608, SPB-608, Rtx-35, or equivalent.

6.21.2.2 30 m x 0.53 mm ID, 1.0 µm film thickness, DB-1701, or equivalent.

6.21.2.3 30 m x 0.53 mm ID, 1.5 µm film thickness, DB-5, SPB-5, Rtx-5, or equivalent.

NOTE: The column length stated above is the minimum requirement. Longer columns that meet resolution and calibration requirements may be used. A description of the GC columns used for analysis shall be provided in the SDG Narrative.

6.21.3 **PACKED COLUMNS CANNOT BE USED**.

6.21.4 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with identification and quantitation of the compounds listed in Exhibit C (Aroclors).
- The analytical results generated using the column meet the initial calibration and calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Aroclors).
- The column pair chosen must have dissimilar phases [choose only one column from each list (i.e., one from 6.21.2.1, one from 6.21.2.2, etc.)].

6.21.5 Although the instructions included in the analytical method are for wide bore capillary columns, narrower bore capillary columns may be evaluated for use. Follow the manufacturer's instructions for use of

its product. Document in the SDG Narrative if other columns are used by specifying the column used.

6.21.6 The Contractor must maintain documentation verifying that the column met the criteria in Section 6.21.4. The minimum documentation is as follows:

6.21.6.1 Manufacturer-provided information concerning the performance characteristics of the column.

6.21.6.2 Chromatograms and data system reports for initial calibration, calibration verification standard, and blanks that are generated on the GC/Electron Capture Detector (ECD) and used for Contract Laboratory Program (CLP) analyses.

6.21.6.3 Based on the Contractor-generated data described in Section 6.21.6.2, the Contractor must complete a written review, signed by the Laboratory Manager, certifying that:

- The column performance is comparable to the required column performance in its ability to produce initial calibration and calibration verifications that meet the technical acceptance criteria in Sections 9.2.5 and 9.3.5.

- The column does not introduce contaminants that interfere with identification and quantitation of compounds listed in Exhibit C (Aroclors).

6.21.6.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request by the USEPA Regional CLP Project Officer (CLP PO).

6.21.7 Columns are mounted in a press-fit Y-shaped glass 3-way union splitter or a Y-shaped fused-silica connector from a variety of commercial sources. The two columns may be mounted in an 8 inch deactivated glass injection tee. The Contractor should follow the manufacturer's recommendations for mounting 0.53 mm capillary columns in injector ports.

6.21.8 The carrier gas for routine applications is helium. The Contractor may choose to use hydrogen as a carrier gas, but they must clearly identify its use in the SDG Narrative and on all divider pages preceding raw chromatographic data in submissions to USEPA. Use of a hydrogen leak detector is highly recommended when hydrogen is used as the carrier gas. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.22 Electron Capture Detector (ECD)

The linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. The make-up gas must be P-5, P-10 (argon/methane), or nitrogen according to the instrument specification. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector. The GC/ECD system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants that may interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.23 Data System

A data system must be interfaced to the GC/ECD. The data system must allow the continuous acquisition of data throughout the duration of the chromatographic program and must permit, at a minimum, the output of time vs. intensity (peak height or peak area) data. Also, the data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method.

6.24 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1.1 Reagent Water - Reagent water is defined as water in which an interferent is not observed at or above the Contract Required Quantitation Limit (CRQL) for each analyte of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon.

7.1.1.2 Reagent water may be generated using a water purification system.

7.1.2 Sodium Sulfate - Granular-anhydrous reagent grade, heated at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

7.1.3 Sulfuric Acid Solution - Prepare a 1:1 (v/v) solution by slowly adding 50 mL of sulfuric acid (sp. gr. 1.84) to 50 mL of reagent water.

7.1.4 Sodium Hydroxide Solution (10 N) - Carefully dissolve 40 g of sodium hydroxide in reagent water and dilute the solution to 100 mL.

7.1.5 Phosphoric Acid Solution - Prepare a 1:1 (v/v) solution of 85% phosphoric acid in reagent water.

7.1.6 Acetone/hexane (1:1 v/v).

7.1.7 Acetone/methylene chloride (1:1 v/v).

7.1.8 Methylene chloride, hexane, acetone, toluene, iso-octane, 2-propanol, cyclohexane, acetonitrile, n–butyl chloride, and methanol (optional). It is recommended that each lot of solvent used be analyzed to demonstrate that it is free of interference before use. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene

chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions (1000 mg/L)

7.2.2.1 Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions.

7.2.2.2 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in iso-octane or hexane and dilute to volume in a 10 mL volumetric flask. Larger volumes may be used at the convenience of the Contractor.

7.2.2.3 When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution. If the compound purity is assayed to be less than 96%, the weight must be corrected when calculating the concentration of the stock solution (see Exhibit E, Section 7).

7.2.2.4 Fresh stock standards must be prepared once every 6 months, or sooner if standards have degraded or concentrated. Stock standards must be checked for signs of degradation or concentration just prior to preparing working standards from them.

7.2.2.5 Commercially-prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.2.3 Secondary Dilution Standards

7.2.3.1 Using stock standards, prepare secondary dilution standards in iso-octane or hexane that contain the compounds of interest either singly or mixed together.

7.2.3.2 Fresh secondary dilution standards must be prepared once every 6 months, or sooner if standards have degraded or concentrated. Secondary dilution standards must be checked for signs of degradation or concentration just prior to preparing working standards from them.

7.2.4 Working Standards

7.2.4.1 Surrogate Standard Spiking Solution

The surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to all standards, samples [including Laboratory Control Samples (LCSs)], Matrix Spike/Matrix Spike Duplicates (MS/MSDs), Performance Evaluation (PE) samples (if required), and blanks prior to extraction. Prepare a surrogate spiking solution of 0.80 µg/mL of each of the two compounds in acetone. The solution

should be checked frequently for stability. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

7.2.4.2 Matrix Spiking Solution

Prepare a matrix spiking solution of 0.8 µg/mL of Aroclor 1016 and Aroclor 1260 in acetone or methanol. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

7.2.4.3 Laboratory Control Sample (LCS) Spiking Solution

Prepare an LCS spiking solution of 0.8 µg/mL of Aroclor 1016 and Aroclor 1260 in acetone or methanol. The LCS solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.4.4 Calibration Standards for Aroclors

Aroclor standards must be prepared individually, except for Aroclor 1260 and Aroclor 1016 which may be combined in one standard mixture.

7.2.4.4.1 Prepare a five-point initial calibration standard solution containing a mixture of Aroclors 1016 and 1260 at the following levels: 20; 40; 80; 160; and 320 µg/L. Also, prepare a single-point initial calibration standard solution containing Aroclor 1221 at 40 µg/L and Aroclors 1232, 1242, 1248, and 1254 at 20 µg/L. These solutions must be prepared in hexane or iso-octane.

7.2.4.4.2 Prepare a single-point calibration verification standard solution containing Aroclor 1260 and Aroclor 1016 at 80 µg/L.

7.2.4.4.3 If Aroclor 1221, 1232, 1242, 1248, 1254 are detected in a sample, then a five-point initial calibration solution for the detected Aroclor must be prepared at the following levels: Aroclor 1221 at 40, 60, 120, 240, and 480 µg/L and Aroclors 1232, 1242, 1248, 1254 at 20, 40, 80, 160, and 320 µg/L. These solutions must be prepared in hexane or iso-octane.

7.2.4.5 GPC Calibration Solution

7.2.4.5.1 Prepare a GPC calibration solution in methylene chloride that contains the following analytes at the minimum concentrations listed below. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Analyte	Concentration (mg/mL)
Corn oil	25.0
Bis(2-ethylhexyl)phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

7.2.5 Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained 2 years from the preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.2 - 7.3 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (Section 7.3.5).

7.3 Storage of Standard Solutions

7.3.1 Store the stock and secondary standard solutions at 4°C (±2°C) in polytetrafluoroethylene (PTFE)-lined, screw-cap, amber bottles/vials.

7.3.2 Store the working standard solutions at 4°C (±2°C) in PTFE-lined screw-cap, amber bottles/vials. The working standards must be checked frequently for signs of degradation or evaporation.

NOTE: Refrigeration may cause the corn oil in the GPC calibration solution to precipitate. Before use, allow the GPC calibration solution to stand at room temperature until the corn oil dissolves.

7.3.3 Protect all standards from light.

7.3.4 Samples, sample extracts, and standards must be stored separately.

7.3.5 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use.

NOTE: Storage of standard solutions in the freezer may cause some compounds to precipitate. This means that at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked to verify that all components have remained in solution. Additional steps may be necessary to ensure that all components are in solution.

7.4 Temperature Records for Storage of Standards

7.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with screw-caps lined with polytetrafluoroethylene (PTFE). If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the USEPA Region.

8.1.2 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 4°C (±2°C) until 365 days after delivery of a complete, reconciled data package to USEPA.

8.3.2 Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3.3 Samples, sample extracts, and standards must be stored separately.

8.4 Records for Sample and Sample Extract Storage

8.4.1 The temperature of all sample and sample extract storage refrigerators shall be recorded daily.

8.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.5 Contract Required Holding Times

8.5.1 Extraction of water samples by separatory funnel procedures must be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of water samples by continuous liquid-liquid extraction (CLLE) procedures must be completed within 5 days of the VTSR. Extraction of soil/sediment samples must be completed within 10 days of the VTSR.

8.5.2 As part of USEPA’s Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) samples as standard extracts that the Contractor is required to prepare per instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the

samples in the Sample Delivery Group (SDG). The extraction holding time (5 days after the VTSR for water, 10 days after the VTSR for soil/sediment) do not apply for PE samples received as standard extracts.

8.5.3 Analysis of sample extracts must be completed within 40 days following the start of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Gas Chromatograph (GC) Operation Conditions

9.1.1 The following are the gas chromatographic analytical conditions for a wide-bore capillary column. The conditions are recommended unless otherwise noted.

Column Conditions	0.5/1.0 um film thickness	1.5 um film thickness
Carrier gas (He)	5-7 mL/min.	6 mL/min.
Make-up gas [argon/methane (P-5 or P-10) or N2]	30 mL/min.	30 mL/min.
Injector temperature	205°C	205°C
Detector temperature	290°C	290°C
Initial temperature	150°C, hold 0.5 min.	140°C, hold 2 min.
Temperature program	150°C to 270°C at 5°C/min.	140°C to 240°C at 10°C/min., hold 5 min. at 240°C, 240°C to 265°C at 5°C/min.
Final temperature	270°C, hold 10 min.	265°C, hold 18 min.

9.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, and samples including Laboratory Control Samples (LCSs) and Matrix Spike/Matrix Spike Duplicates (MS/MSDs). The linearity of the Electron Capture Detector (ECD) may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

9.1.3 Manual injections must be 2.0 µL. Auto injectors may use 1.0 µL volumes. The same injection volume must be used for all standards, required blanks, and samples (including LCSs and MS/MSDs).

9.2 Initial Calibration

9.2.1 Summary of Initial Calibration

Prior to sample analysis (including LCSs and MS/MSDs) and required blanks, each GC/ECD system must be initially calibrated to determine instrument sensitivity and the linearity of Aroclor response. An initial five-point calibration is performed using Aroclors 1016 and 1260 to demonstrate the linearity of the detector response. The other five Aroclors are calibrated at a single mid-point for pattern recognition. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed

before or after the analysis of the five levels of the Aroclor 1016/1260 standards.

9.2.2 Frequency of Initial Calibration

Each GC/ECD system must be initially calibrated upon award of the contract, whenever major instrument maintenance or modification is performed (e.g., column replacement or repair, cleaning or replacement of the ECD, etc.) or if the calibration verification technical acceptance criteria have not been met.

9.2.3 Procedure for Initial Calibration

9.2.3.1 Set up the GC/ECD systems as described in Section 9.1. Optimize the instrumental conditions for resolution of the target compounds and sensitivity.

NOTE: Once the GC conditions have been established, the same operating conditions must be used for both calibrations and sample analyses.

9.2.3.2 Prepare the initial calibration standards using the analytes and the concentrations specified in Sections 7.2.4.4.1 and 7.2.4.4.2.

9.2.3.3 If Aroclors other than Aroclor 1016/1260 are detected in an analysis, a separate five-point calibration must be prepared (Section 7.2.4.4.3) and run for that particular Aroclor.

9.2.3.4 All standards, blanks, samples, LCSs, MS/MSDs, and extracts must be allowed to warm to ambient temperature before analysis.

9.2.3.5 Analyze the initial calibration sequence as given below.

NOTE: The single-point Aroclor standards may be analyzed after the analysis of the five levels of the Aroclor 1016/1260 standards.

Initial Calibration Sequence

1. Aroclor 1221
2. Aroclor 1232
3. Aroclor 1242
4. Aroclor 1248
5. Aroclor 1254
6. Aroclor 1016/1260 (20 µg/L)
7. Aroclor 1016/1260 (40 µg/L)
8. Aroclor 1016/1260 (80 µg/L)
9. Aroclor 1016/1260 (160 µg/L)
10. Aroclor 1016/1260 (320 µg/L)

9.2.4 Calculations for Initial Calibration

9.2.4.1 During the initial calibration sequence, absolute Retention Times (RTs) are determined for each surrogate and between 3-5 major peaks of each Aroclor.

9.2.4.2 For Aroclors 1016 and 1260, an RT is measured for each of the 3-5 peaks in each of the five calibration standards and the mean RT ($\overline{RT}$) is calculated for each of the 3-5 peaks as the average of the five values obtained from the five calibration standards. For Aroclors 1221, 1232, 1242, 1248, and 1254, an RT is measured for each of the 3-5 peaks for a single-point calibration standard, if a valid five-point calibration is present for a specific Aroclor then an RT is measured for each of the 3-5 peaks in each of the five calibration standards and the $\overline{RT}$ is calculated as the average of the five values for each of the 3-5 peaks obtained from the five calibration standards. An RT is measured for the surrogates in each of the five calibrations and the ($\overline{RT}$) is calculated as the average of the five values. Calculate the ($\overline{RT}$) using Equation 1:

EQ. 1 Mean Retention Time

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

Where,

$\overline{RT}$ = Mean absolute Retention Time of analyte.

RT_i = Absolute Retention Time of analyte.

n = Number of measurements.

9.2.4.3 An RT window is calculated for the major peaks (3-5) of each Aroclor and for each surrogate using the RT window listed below. Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.

Compounds	Retention Time Windows (minutes)
Aroclors	±0.07
tetrachloro-m-xylene	±0.05
decachlorobiphenyl	±0.10

9.2.4.4 The linearity of the instrument is determined by calculating a Percent Relative Standard Deviation (%RSD) of the Calibration Factors (CFs). Either peak area or peak height may be used to calculate CFs used in the %RSD equation.

Five sets of CFs will be generated for the Aroclor 1016/1260 mixture, each set consisting of the CFs for each of the five peaks chosen for this mixture. The single standard for each of the other Aroclors will generate at least three CFs, one for each

selected peak, unless a valid five-point calibration is present for a specific Aroclor, in which case five sets of CFs will be generated for the specific Aroclor.

Calculate CFs, the Mean CF (**66**), and the %RSD of the CFs for each peak in a selected set of 3-5 major peaks for each Aroclor using Equations 2, 3, and 4.

EQ. 2 Calibration Factor Calculation

$$CF = \frac{\text{Peak area (or Height) of the standard}}{\text{Mass Injected (ng)}}$$

EQ. 3 Mean Calibration Factor Calculation

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

EQ. 4 Percent Relative Standard Deviation Calculation

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

Where,

SD_{CF} =

$$\sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{(n-1)}}$$

%RSD = Percent Relative Standard Deviation.

SD_{CF} = Standard Deviation of Calibration Factors.

CF_i = Calibration Factor.

66 = Mean Calibration Factor.

n = Total number of values.

9.2.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to both GC columns.

9.2.5.1 The initial calibration sequence must be analyzed according to the procedure listed in Section 9.2.3, at the concentrations listed in

Section 7.2.4.4, and at the frequency listed in Section 9.2.2. The GC/ECD operating conditions optimized in Section 9.1 must be followed.

9.2.5.2 The identification of Aroclors by GC methods is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for Aroclors.

- The chromatograms of the standards for the Aroclors analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25% and less than 100% of full scale.
- If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram. Both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

9.2.5.3 The %RSD for each Aroclor peak and surrogates must be less than or equal to 20%. The %RSD requirement applies to any other Aroclor analyzed at the five-point calibration (if required in Section 9.2.3.3).

9.2.6 Corrective Action for Initial Calibration

9.2.6.1 If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, bake-out the detector, clean the injection port, or take other corrective actions to achieve the acceptance criteria.

9.2.6.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. In the case of low-level contamination, baking out the detector at an elevated temperature (350°C) should be sufficient to achieve acceptable performance. In the case of heavy contamination, passing hydrogen through the detector for 1-2 hours at an elevated temperature may correct the problem. In the case of severe contamination, the detector may require servicing by the ECD manufacturer.

CAUTION: DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.

9.2.6.3 If a laboratory cleans out a detector using an elevated temperature, the ECD electronics must be turned off during the bake-out procedure.

9.2.6.4 After bake-out or hydrogen reduction, the detector must be recalibrated using the initial calibration sequence.

9.2.6.5 Initial calibration technical acceptance criteria must be met before any sample, including MS/MSD, LCS, or required blanks, are analyzed. Any samples or required blanks analyzed before the initial calibration technical acceptance criteria have been met will require reanalysis at no additional cost to USEPA.

9.3 Calibration Verification

9.3.1 Summary of Calibration Verification

A calibration verification standard is used to verify the calibration and evaluate instrument performance. Aroclors 1016/1260 constitute the calibration verification. Sample data are not acceptable unless bracketed by acceptable analysis of the calibration verification standard.

9.3.2 Frequency of Calibration Verification

9.3.2.1 An Aroclor 1016/1260 standard must be analyzed each 12-hour shift prior to conducting any sample analyses. Analysis of this calibration standard is required at the end of the analysis sequence. It is not required to analyze other Aroclor standards besides Aroclor 1016/1260 as calibration verification, unless another Aroclor was detected (see Section 9.2.3.3).

9.3.2.2 The requirements for running the calibration verification is waived when no samples (including LCSs and MS/MSDs), dilutions, reanalyses, method blanks, and Aroclors are analyzed during that 12-hour period. To resume analysis, using the existing initial calibration, the Contractor first must analyze a calibration verification standard that meets the technical acceptance criteria.

9.3.3 Procedure for Calibration Verification

9.3.3.1 Analyze the Aroclor 1016/1260 standard at the required frequencies (Section 9.3.2).

9.3.3.2 Prepare the calibration verification standard using the Aroclor 1016/1260 standard at the concentrations specified in Section 7.2.4.4.2.

9.3.3.3 All standards must be at ambient temperature at the time of preparation and analysis.

9.3.4 Calculations for Calibration Verification

9.3.4.1 For each analysis of the Aroclor 1016/1260 standard used to demonstrate calibration verification, calculate the Percent Difference (%Difference) between the CF for each Aroclor peak in the calibration verification standard and the 66 from the initial calibration curve using the following equation:

EQ. 5 Percent Difference Calculation

$$\%Difference = \frac{CF - \overline{CF}}{\overline{CF}} \times 100$$

Where,

%Difference = Percent Difference.

CF = Calibration Factor.

$\overline{CF}$ = Mean Calibration Factor.

9.3.5 Technical Acceptance Criteria for Calibration Verification

All calibration verification technical acceptance criteria apply independently to each column, and must meet criteria specified in Section 9.2.5.2.

9.3.5.1 The Aroclor 1016/1260 standards must be analyzed at the required frequency on a GC/ECD system that has met the initial calibration technical acceptance criteria.

9.3.5.2 The absolute RT of each of the Aroclor peaks and surrogates in the calibration verification standard must be within the RT window determined from the initial calibration standard in Section 9.2.4.3.

9.3.5.3 The CF for each Aroclor peak and surrogates calculated from the calibration verification standard must not exceed a difference of more than ±15% when compared to the $\overline{CF}$ from the initial calibration curve.

9.3.6 Corrective Action for Calibration Verification

9.3.6.1 If the technical acceptance criteria for the calibration verification are not met, inspect the system for problems and take corrective action to achieve the acceptance criteria.

9.3.6.2 Major corrective actions such as replacing the GC column or baking out the detector will require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.2.5.

9.3.6.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard that originally failed the criteria does meet all the acceptance criteria.

9.3.6.4 If the Aroclor 1016/1260 standard does not meet technical acceptance criteria listed in Sections 9.3.5.2 and 9.3.5.3, it must be re-injected immediately. If the second injection of the Aroclor 1016/1260 standard meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration sequence must be run before more sample data are collected.

9.3.6.5 The Contractor is reminded that running an Aroclor 1016/1260 standard once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run standards more often to avoid discarding data.

9.3.6.6 Calibration verification technical acceptance criteria must be met before any sample, including MS/MSD and LCS is reported. Any samples, including MS/MSDs, LCSs, and required blanks associated with a calibration verification that do not meet the technical acceptance criteria will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

The Contractor must have the capability to perform all of the sample cleanup procedures presented in this Exhibit, including those included by reference. The Contractor may use any of the procedures or combinations of procedures to cleanup the samples prior to analysis, unless the Contractor is specifically directed by the Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including Method Detection Limits (MDLs) and any precision and recovery limits.

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region’s decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 Multi-Phase Samples

If multi-phase samples (e.g., a two-phase liquid sample, oily, sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region.

10.1.2.1 If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample;
- Separate the phases of the sample and analyze each phase separately. SMO will provide EPA Sample Numbers for the additional phases, if required;
- Separate the phases and analyze one or more of the phases, but not all of the phases. SMO will provide EPA Sample Numbers for the additional phases, if required; or
- Do not analyze the sample.

10.1.2.2 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phase(s) and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA Sample Numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.3 No other change in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Extraction of Water Samples

Water samples may be extracted by either a separatory funnel procedure or a continuous liquid-liquid extraction (CLLE) procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, CLLE must be employed. Allow the samples to warm to ambient temperature.

10.1.3.1 Separatory Funnel Extraction (SFE)

10.1.3.1.1 Measure out each 1 L sample aliquot in a separate graduated cylinder. Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the SDG Narrative. Place the sample aliquot into a 2 L separatory funnel.

10.1.3.1.2 Using a syringe or a volumetric pipet, add 1 mL of the surrogate solution (Section 7.2.4.1) to all water samples.

10.1.3.1.3 Rinse the graduated cylinder with 30 mL of methylene chloride and transfer the rinsate to the separatory funnel. If the sample container is empty, rinse the container with 30 mL of methylene chloride and add the rinsate to the separatory funnel. If the sample container is not rinsed, then add another 30 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 min., with periodic venting to release excess pressure.

NOTE: The total volume of solvent used for extraction is 60 mL. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration through glass wool, centrifugation, or other physical means. Drain the methylene chloride into a 250 mL Erlenmeyer flask.

10.1.3.1.4 Add a second 60 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Proceed to Section 10.1.5.

10.1.3.2 Continuous Liquid-Liquid Extraction (CLLE)

10.1.3.2.1 CLLE Without Hydrophobic Membrane

10.1.3.2.1.1 Follow manufacturer's instructions for set-up.

10.1.3.2.1.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least one inch above the bottom sidearm.

10.1.3.2.1.3 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure the pH of the sample with wide range pH paper or a pH meter and record the pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring the pH adjustment must be noted in the SDG Narrative.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.1.4 Using a syringe or volumetric pipet, add 1 mL of the surrogate standard spiking solution (Section 7.2.4.1) into the sample and mix well.

10.1.3.2.1.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.2.1.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/min (recommended); optimize the extraction drip rate. Extract for a <u>minimum</u> of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/min is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.1.5.

NOTE 2: Some continuous extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.2.2 CLLE With Hydrophobic Membrane

10.1.3.2.2.1 Follow the procedure in Sections 10.1.3.2.1, but reduce the amount of methylene chloride used to 50 mL and extract for a <u>minimum</u> of 6 hours.

10.1.3.2.2.2 Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the

solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to ensure efficient extraction of the sample, and extend the extraction time by a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used. Proceed to Section 10.1.5.

NOTE 1: It may not be necessary to dry the extract with sodium sulfate if the hydrophobic membrane type extractor is used.

NOTE 2: If low surrogate recoveries occur, assure that: 1) the apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling was optimized; and 3) there was proper cooling for condensation of solvent.

NOTE 3: Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the manufacturer's instructions for set-up.

10.1.4 Soil/Sediment Samples

Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase.

10.1.4.1 pH Determination

Transfer 50 g of soil/sediment to a 100 mL beaker. Add 50 mL of water and stir the solution with a magnetic stirrer for 1 hour. Determine the pH of the sample by using a combination glass electrode and pH meter while the sample is stirred. Report the pH value on the appropriate data sheet. If the pH of the soil/sediment is greater than 9 or less than 5, document any subsequent problems in the analysis related to pH in the SDG Narrative, but do not attempt to adjust the pH of the sample. Discard the portion of the sample used for pH determination.

NOTE: If insufficient volume of soil/sediment is received, use a smaller 1:1 ratio of grams of sample to milliliters of water for the pH determination, and note in the SDG Narrative.

10.1.4.2 Percent Moisture (%Moisture)

Weigh 5-10 g of the soil/sediment to the nearest 0.01 g into a tarred crucible or aluminum weighing pan. Determine the weight percent volatilized (hereafter referred to as Percent Moisture) by drying overnight at 105°C. After the sample is dry, remove the sample and pan and allow them to cool in a desiccator before weighing. Calculate the Percent Moisture according to Equation 6 below. Concentrations of individual analytes will be reported relative to the dry weight of soil/sediment.

CAUTION: Gases volatized from some soil/sediment samples may require that this drying procedure be carried out in a hood.

EQ. 6 Percent Moisture Calculation

$$\%\text{Moisture} = \frac{\text{grams of wet sample} - \text{grams of dry sample}}{\text{grams of wet sample}} \times 100$$

10.1.4.3 Extraction of Soil/Sediment Samples

10.1.4.3.1 Three procedures are provided for the extraction of Aroclor compounds from soil/sediment samples:

- Ultrasonic extraction;
- [Automated] Soxhlet extraction; and
- Pressurized fluid extraction.

The Contractor shall use one of the above procedures for the extraction of soil/sediment samples.

NOTE: All soil/sediment samples in a Case must be extracted by the same procedure.

10.1.4.3.2 For soil/sediment extractions, weigh approximately 30 g of sample, to the nearest 0.1 g, into a 400 mL beaker. Add 60 g of anhydrous powdered or granulated sodium sulfate, or sufficient quantity and mix well. Proceed to Section 10.1.4.3.3 for ultrasonic extraction, Section 10.1.4.3.4 for automated Soxhlet extraction, or Section 10.1.4.3.5 for pressurized fluid extraction. As applicable, follow the manufacturer's instructions for use of all extraction equipment.

10.1.4.3.3 Ultrasonic Extraction

10.1.4.3.3.1 Add 1 mL of the surrogate standard spiking solution (Section 7.2.4.1) to the sample, then immediately add 100 mL of 1:1 (v/v) acetone/methylene chloride.

10.1.4.3.3.2 Place the bottom surface of the tip of the 3/4 inch tapered disruption horn about 1/2 inch below the surface of the solvent, but above the sediment layer. Do <u>not</u> use a microtip probe.

10.1.4.3.3.3 Sonicate for 3 min. with the output control knob set at 10 (full power), mode switch on Pulse, and the percent duty cycle knob set at 50.0%.

NOTE: These settings refer to Model W-385. When using a sonicator other than Model W-385, refer to the manufacturer's instructions for appropriate output settings.

10.1.4.3.3.4 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.1.4.3.3.5 Repeat the extraction two more times with two additional

100 mL portions of 1:1 (v/v) acetone/methylene chloride. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or, very carefully, with the tip of the unenergized probe. Decant the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.1.5.

10.1.4.3.4 [Automated] Soxhlet Extraction

Contractor may use either automated or non-automated Soxhlet extraction. The following procedure is based on the use of a Soxtec HT-6 automated Soxhlet extraction system. When using a different system, refer to the instructions provided by the manufacturer for the appropriate procedure.

10.1.4.3.4.1 Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/min to prevent solvent loss through the condensers.

10.1.4.3.4.2 Transfer the entire sample from the beaker (Section 10.1.4.3.2) to the thimble. Add 1 mL of the surrogate standard spiking solution (Section 7.2.4.1) to the sample.

10.1.4.3.4.3 Immediately transfer the thimbles containing the samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

10.1.4.3.4.4 Insert the extraction cups containing boiling chips, and load each with an appropriate volume of extraction solvent 1:1 (v/v) acetone/methylene chloride. Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position.

NOTE: The seals must be pre-rinsed or preextracted with extraction solvent prior to initial use.

10.1.4.3.4.5 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 min. The condenser valves must be in the "OPEN" position. Extract for the preset time.

10.1.4.3.4.6 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set the timer for 60 min. Make certain that condenser valves are still open. Extract for the preset time. After the rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

10.1.4.3.4.7 When all but 2-5 mL of solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the

cups using methylene chloride and add the rinsates to the glass tubes. Proceed to Section 10.1.5.

10.1.4.3.5 Pressurized Fluid Extraction

10.1.4.3.5.1 Transfer the entire sample from the beaker (Section 10.1.4.3.2) to an extraction cell of the appropriate size for the aliquot. Add 1 mL of the surrogate standard spiking solution (Section 7.2.4.1) to the sample.

10.1.4.3.5.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.4.3.5.3 Place a precleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

10.1.4.3.5.4 The following are recommended extraction conditions:

Oven temperature	100°C
Pressure	1500-2000 psi
Static time	5 min. (after 5 min. pre-heat equilibration)
Flush volume	60% of the cell volume
Nitrogen purge	60 sec. at 150 psi (purge time may be extended for larger cells)
Static cycles	1

10.1.4.3.5.5 Optimize the extraction conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice.

10.1.4.3.5.6 Once established, the same pressure should be used for all samples in the same SDG.

10.1.4.3.5.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete. Proceed to Section 10.1.5.

10.1.5 Extract Concentration

10.1.5.1 Concentration by Kuderna-Danish (K-D)

Assemble a K-D concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if

equivalency is demonstrated for all the Aroclors listed in Exhibit C (Aroclors).

10.1.5.1.1 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.

10.1.5.1.2 For soil/sediment samples, directly transfer the extract to the K-D concentrator.

10.1.5.1.3 Rinse the Erlenmeyer flask (for both water and soil/sediment samples) and the column (for water samples) with at least two 20-30 mL portions of methylene chloride to complete the quantitative transfer.

10.1.5.1.4 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-30 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5 mL for water samples (and less than 10 mL for soil/sediment samples), remove the K-D apparatus. Allow it to drain and cool for at least 10 min. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.1.5.1.5 For both water and soil/sediment extracts that do not require GPC cleanup, proceed with the hexane exchange described in Section 10.1.5.2.

10.1.5.1.6 For water extracts that require GPC cleanup, remove the Snyder column, rinse the flask and its lower joint, collect the rinsate in the concentrator tube, and adjust the volume to 10 mL with methylene chloride. Proceed to Section 10.2.1 for GPC cleanup.

10.1.5.1.7 For soil/sediment extracts that require GPC cleanup, it is absolutely necessary to further reduce the volume of all soil/sediment extracts to 1 mL in order to remove most of the acetone. This is best accomplished using the nitrogen evaporation technique (Section 10.2.3.2). The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during the GPC cleanups. Adjust the soil/sediment extract volume to 10 mL with methylene chloride. Proceed to Section 10.2.1 for GPC cleanup.

10.1.5.2 Solvent Exchange into Hexane

This procedure applies to both extracts of water samples and extracts of soil/sediment samples.

10.1.5.2.1 With the extract in a K-D apparatus, remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as

described in Section 10.1.5.1, but increase the temperature of the water bath (80-90°C recommended) to maintain proper distillation.

10.1.5.2.2 Remove the Snyder column; using 1-2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Complete quantitative transfer of the extract to a 10 mL vial by using hexane.

10.1.5.2.3 For samples that have not been subjected to Gel Permeation Chromatography (GPC) cleanup, adjust the volume of the hexane extract to 10 mL. For samples that have been subjected to GPC cleanup, concentrate the hexane extract to 5 mL using a Micro Snyder Column or nitrogen evaporation, as described in Section 10.1.5.3.1 or 10.1.5.3.2, then proceed to Section 10.2.2 for sulfuric acid cleanup.

10.1.5.3 Final Concentration of Extract

Two different techniques are permitted to concentrate the extract to volume before cleanup or instrumental analysis. They are the Micro Snyder Column and Nitrogen Evaporation Technique.

10.1.5.3.1 Micro Snyder Column Concentration

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath (80-90°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 min. while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.2 mL of hexane. If GPC cleanup is needed and not yet performed adjust the volume to 10 mL with methylene chloride and proceed to Section 10.2.1 for GPC cleanup. For samples that do not require GPC cleanup adjust the volume to 10 mL with hexane and proceed to Section 10.2.2 for sulfuric acid cleanup. For samples that have already undergone GPC cleanup adjust the volume with hexane to 5 mL and proceed to Section 10.2.2 for sulfuric acid cleanup. If no further cleanup is needed adjust the volume with hexane to the same volume of the aliquot used for sulfuric acid cleanup (1 or 2 mL) and proceed to Section 10.3 for GC/ECD analysis.

10.1.5.3.2 Nitrogen Evaporation Technique (taken from ASTM Method D 3086)

10.1.5.3.2.1 Place the Concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to the final volume by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) onto the solvent. DO NOT ALLOW THE EXTRACT TO GO DRY. If GPC cleanup is needed and not yet performed adjust the volume to 10 mL with methylene chloride and proceed to Section 10.2.1 for GPC cleanup. For samples that do not require GPC cleanup

adjust the volume to 10 mL with hexane and proceed to Section 10.2.2 for sulfuric acid cleanup. For samples that have already undergone GPC cleanup adjust the volume with hexane to 5 mL and proceed to Section 10.2.2 for sulfuric acid cleanup. If no further cleanup is needed adjust the volume with hexane to the same volume of the aliquot used for sulfuric acid cleanup (1 or 2 mL) and proceed to Section 10.3 for GC/ECD analysis.

10.1.5.3.2.2 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or polytetrafluoroethylene (PTFE) tubing. Plastic tubing must not be used between the carbon trap and the sample as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane and then dried prior to use.

10.1.5.3.2.3 During evaporation, the tube solvent level must be kept below the water level of the bath.

10.2 Cleanup Procedures

There are two cleanup procedures specified in the method: GPC cleanup and sulfuric acid cleanup. GPC cleanup is optional for water and soil/sediment extracts. Sulfuric acid cleanup is mandatory for all extracts. Method blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them. The following may be used in addition to those described here, so long as all technical acceptance criteria are met: SW-846 Methods 3610B (Alumina); 3630C (Silica Gel); and 3650B (Acid/Base Partition).

10.2.1 GPC Cleanup

10.2.1.1 Introduction

GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of natural (and synthetic) macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated.

10.2.1.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternate column packings may be used if 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the Aroclor compounds. Follow the manufacturer's instructions for preparation of the GPC column.

10.2.1.3 Calibration of GPC

10.2.1.3.1 Summary of GPC Calibration

10.2.1.3.1.1 The GPC calibration procedure is based on monitoring the elution of standards with an ultraviolet (UV) detector connected to the GPC column.

10.2.1.3.1.2 The UV detector calibration procedure described in Section 10.2.2.3.3 is needed for the analyses of Aroclors listed in Exhibit C (Aroclors). IT MUST NOT BE USED FOR THE ANALYSIS OF GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS) EXTRACTABLES OR OTHER ANALYTES WITHOUT A RECOVERY STUDY.

10.2.1.3.2 Frequency of GPC Calibration

Each GPC system must be calibrated upon award of the contract, when the GPC calibration fails to meet acceptance criteria (Section 10.2.2.3.4), when the column is changed, when channeling occurs, and once every 7 days. Also, the Retention Time (RT) shift must be less than 5% when compared to RTs in the last calibration UV traces.

10.2.1.3.3 Procedure for GPC Calibration

Follow the manufacturer's instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte RTs and must be monitored.

10.2.1.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.4) onto the GPC. Determine the elution times for the phthalate, methoxychlor, and perylene. Phthalate will elute first; perylene will elute last.

Choose a "DUMP" time that removes greater than 85% of the phthalate. Choose a "COLLECT" time so that greater than 95% of the methoxychlor is collected, and continue to collect until just prior to the elution time of sulfur. Use a "WASH" time of 10 min.

NOTE: The "DUMP" and "COLLECT" times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

10.2.1.3.3.2 Re-inject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

10.2.1.3.3.3 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

10.2.1.3.3.4 Analyze a GPC blank of methylene chloride. Concentrate the methylene chloride that passed through the system during the collect cycle using a K-D evaporator. Exchange the solvent to hexane and analyze the concentrate by GC/ECD according to the procedure in Section 10.1.5 (usual protocol). If the blank exceeds the estimated quantitation limit of the analytes, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping, if necessary.

10.2.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.2.1.3.4.1 The GPC system must be calibrated at the frequency described in Section 10.2.1.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution;
- Corn oil and phthalate peaks must exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks must exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks must exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and must exhibit greater than 90% baseline resolution.

10.2.1.3.4.2 The solvent flow rate and column pressure must be within the manufacturer's specified ranges.

10.2.1.3.4.3 The RTs for bis (2-ethylhexyl) phthalate and perylene must not vary more than ±5% between calibrations. Excessive RT shifts are caused by the following:

- Poor laboratory temperature control or system leaks;
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight; and/or
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.2.1.3.5 Corrective Action for GPC Calibration

10.2.1.3.5.1 If the flow rate and/or column pressure do not fall within the manufacturer's specified ranges, a new column should be prepared.

10.2.1.3.5.2 A UV trace that does not meet the criteria in Section 10.2.2.3.4 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.2.1.3.5.3 If the GPC blank is equal to or exceeds the Contract Required Quantitation Limit (CRQL) of any compound in Exhibit C (Aroclors), pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.2.1.4 Daily UV Calibration Check (Optional)

The calibration of the GPC may be monitored daily by use of the UV-GPC calibration solution (Section 7.2.4) and the UV detector calibration procedure (Section 10.2.2.3.3). The UV detector should be used to monitor the elution times for the phthalate,

methoxychlor and perylene, in that order. The precalibrated GPC program should "DUMP" greater than 85% of the phthalate and should "COLLECT" greater than 95% of the methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., >0.5 min.) indicate that the column is out of calibration and must be recalibrated or replaced.

10.2.1.5 Sample Cleanup by GPC

10.2.1.5.1 Introduction to Sample Cleanup by GPC

10.2.1.5.1.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, RTs will shift, and the dump and collect times determined by the calibration standard no longer will be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C.

10.2.1.5.1.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of 1:1 (v/v) glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 40 mg/mL of non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tarred aluminum weighing pan, or other suitable container. When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected.

10.2.1.5.1.3 Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is injected onto the column. Viscous extracts, or extracts containing a large amounts of non-volatile residue, will cause problems with injecting the proper amount of sample extract onto the column using automated injection systems. After the sample extract has been processed, the remaining sample extract in an injection vial must be checked to assure that the proper amount of extract was injected on the column before proceeding with the sample analysis. If the proper amount of extract was not injected, the sample must be reprepared and the sample extract must be either diluted and loaded into several loops or the sample extract must be injected manually.

10.2.1.5.2 Frequency of Sample Cleanup by GPC

If required, GPC cleanup must be performed at least once for each soil/sediment and water extracts that contain high molecular weight contaminants that interfere with the analysis of the target analytes and all associated QC [blanks, Laboratory Control Samples (LCSs), and Matrix Spike/Matrix Spike Duplicates (MS/MSDs)]. If the cleanup procedure is inadequate, contact SMO.

10.2.1.5.3 Procedure for Sample Cleanup by GPC

10.2.1.5.3.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of

sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap). Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

10.2.1.5.3.2 INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

10.2.1.5.3.3 Follow the manufacturer's instructions for operation of the GPC system being utilized.

NOTE: These instructions were written for a 5 mL GPC injection loop. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL loop is used, concentrate the 10 mL extract to 4 mL, and then inject 2 mL from the 4 mL.

10.2.1.5.3.4 If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action following the manufacturer's recommendations. The problem must be resolved prior to loading sample extracts.

10.2.1.5.3.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.2.1.5.3.6 Collect each sample in a 250 mL Erlenmeyer flask covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure;
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used; and/or
- Leaks in the system or significant variances in room temperature.

10.2.1.5.3.7 After the appropriate GPC fraction has been collected for each sample, concentrate the extract as per Section 10.1.5.1 and proceed to solvent exchange into hexane as described in Section 10.1.5.2.

10.2.1.5.3.8 Any samples that were loaded into two or more loops must be recombined before proceeding with concentration.

10.2.2 Sulfuric Acid Cleanup

10.2.2.1 Sulfuric acid cleanup uses hexane solvent that will be treated with concentrated sulfuric acid. This method is used for rigorous cleanup of sample extracts prior to analysis of Polychlorinated Biphenyls (PCBs). This method is used to provide accuracy in quantitation of Aroclors by eliminating elevated baselines or overly complex chromatograms.

10.2.2.2 Frequency of Sulfuric Acid Cleanup

Sulfuric acid cleanup is required for all water and soil/sediment extracts.

10.2.2.3 Procedure for Sulfuric Acid/Permanganate Cleanup

10.2.2.3.1 Using a syringe or a volumetric pipet, transfer all of the hexane extract to a 10 mL vial and, in a fume hood, carefully add 5 mL of the 1:1 (v/v) sulfuric acid/water solution.

10.2.2.3.2 The volume of hexane extract used depends on the requirements of the Gas Chromatograph (GC) autosampler used by the laboratory. If the autosampler functions reliably with 1 mL of sample volume, 1.0 mL of extract should be used. If the autosampler requires more than 1 mL of sample volume, 2.0 mL of extract should be used.

NOTE: Make sure that there is no exothermic reaction or evolution of gas prior to proceeding.

10.2.2.3.3 Cap the vial tightly and vortex for one min. A vortex must be visible in the vial.

NOTE: Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT AS SULFURIC ACID BURNS.

10.2.2.3.4 Allow the phases to separate for at least 1 min. Examine the top (hexane) layer; it should not be highly colored, nor should it have a visible emulsion or cloudiness.

10.2.2.3.5 If a clean phase separation is achieved, proceed to Section 10.2.2.3.8.

10.2.2.3.6 If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial and dispose of it properly. Add another 5 mL portion of the clean 1:1 (v/v) sulfuric acid/water solution and perform another acid cleanup, beginning at Section 10.2.2.3.7.

NOTE: Do not remove any hexane from the vial at this stage of the procedure.

If the extract is no longer colored, the analyst may proceed to Section 10.2.2.3.11.

10.2.2.3.7 Vortex the sample for 1 min. and allow the phases to separate.

10.2.2.3.8 Transfer the hexane layer to a clean 10 mL vial. Take care not to include any of the acid layer in this clean vial, as it can cause damage to the analytical instrumentation. Once the

hexane layer is removed, perform a second "extraction" of the acid layer, as described in Section 10.2.2.3.9.

10.2.2.3.9 Add an additional 1 mL of hexane to the sulfuric acid layer, cap, and vortex. This second extraction is done to ensure quantitative transfer of the PCBs.

10.2.2.3.10 Remove the second hexane layer and combine with the hexane from Section 10.2.2.3.8.

10.2.2.3.11 Reduce the volume of the combined hexane layers to the original volume (1 mL or 2 mL) using an appropriate concentration technique. Analyze the extract immediately. If analysis of the extract is not performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract is stored longer than 2 days, it should be transferred to a vial with a PTFE-lined screw-cap top, and labeled appropriately.

10.3 GC/ECD Analysis

10.3.1 Introduction

10.3.1.1 Before samples (including LCSs and MS/MSDs) and required blanks (method) can be analyzed, the instrument must meet the initial calibration and calibration verification technical acceptance criteria. All sample extracts, required blanks, and calibration standards must be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions must be allowed to warm to ambient temperature before preparation/analysis. Sample analysis on both GC columns is required for <u>all</u> samples and blanks.

10.3.1.2 Set up the GC/ECD system per the requirements in Section 9.1. Unless ambient temperature on-column injection is used (Section 9.1), the injector must be heated to at least 200°C. The optimized GC conditions from Section 9.1 must be used.

10.3.2 Procedure for Sample Analysis by GC/ECD

The injection must be made on-column by using either automatic or manual injection. If autoinjectors are used, 1 µL injection volumes may be used. Manual injections shall use at least 2 µL injection volumes. The same injection volume must be used for all standards, samples (including LCSs and MS/MSDs), and blanks associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2 µL. However, the same injection volume must be used for all analyses.

10.3.2.1 Analytical Sequence

All acceptable samples must be analyzed within a valid analysis sequence as given below:

Time	Injection #	Material Injected
	1-10	First 10 steps of the initial calibration
0 hr.	11	Aroclor 1016/1260 standard
12 hr		Last sample
	1st injection past 12 hr.	Aroclor 1016/1260 standard
	2nd and 3rd injections past 12 hr.	Subsequent samples
		Last sample
		Aroclor 1016/1260 standard

10.3.2.1.1 The first 12 hours are counted from injection #11, not from injection #1. Samples may be injected until 12:00 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the calibration verification that brackets the front end of the samples. While the 12-hour period may not be exceeded, the laboratory may run standards more frequently, for instance, to accommodate staff working on 8-hour shifts.

10.3.2.1.2 After the initial calibration, the analysis sequence may continue as long as acceptable calibration verification(s) are analyzed at the required frequency. This analysis sequence shows only the minimum required standards. More standards may be run at the discretion of the Contractor; however, the standards must also satisfy the criteria presented in Section 9 in order to continue the run sequence.

10.3.2.1.3 An analysis sequence must also include all samples and required blank analyses, but the Contractor may decide at what point in the sequence they are to be analyzed.

10.3.2.1.4 The requirements for the analysis sequence apply to both GC columns and for all instruments used for these analyses.

10.3.3 Sample Dilutions

10.3.3.1 All samples must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography (defined in Section 11.3).

10.3.3.2 If the response of the largest peak for any Aroclor is greater than the response of the high-point standard in the initial calibration, then the sample must be diluted to have the response of the largest peak be between the low and high calibration standards.

10.3.3.3 If dilution is employed solely to bring a peak within the calibration range or to get an Aroclor pattern on scale, the results for both the more and the less concentrated extracts must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.

10.3.3.4 If the Contractor has reason to believe that diluting the final extracts will be necessary, a less diluted run may still be required. If an acceptable chromatogram (as defined in Section 11.3) is achieved with the diluted extract, then:

- If the Dilution Factor (DF) is greater than 10, an additional extract 10 times more concentrated than the diluted sample extract must be injected and reported with the sample data.
- If the DF is less than or equal to 10, then an undiluted sample extract must be injected and reported with the sample data.

If the analysis of the most concentrated extract does not meet the requirement for dilution in Section 11.3.5, then the analysis is at no additional cost to USEPA.

10.3.3.5 When diluted, Aroclors must be able to be reported at greater than 25.0% of full scale but less than 100.0% of full scale.

10.3.3.6 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram. If the chromatogram of any sample needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

10.3.3.7 Samples with analytes detected at a level greater than the high calibration point must be diluted until the concentration is within the linear range established during calibration or to a maximum of 1:100,000.

10.3.3.8 If the concentration is still above the high calibration standard after the dilution of 1:100,000, the Contractor shall contact SMO immediately.

10.3.3.9 Use the results of the original analysis to determine the approximate DF required to get the largest analyte peak within the initial calibration range.

10.3.3.10 The DF chosen should keep the concentration of the largest peak for an Aroclor in the upper half of the initial calibration range of the instrument.

10.3.3.11 Sample dilutions must be made quantitatively. Dilute the sample extract with hexane.

10.3.3.12 Do not submit data for more than two analyses (i.e., from the original sample extract and one dilution, or, from the most concentrated dilution analyzed and one further dilution). This statement does not refer to reanalyses required due to failed technical acceptance criteria.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The laboratory will identify and quantitate analyte peaks based on the Retention Time (RT) windows and the Calibration Factors (CFs) of each standard established during the initial calibration sequence.

11.1.1.2 Analytes are identified when peaks are observed in the RT window for the analyte on both Gas Chromatograph (GC) columns.

11.1.1.3 A set of 3-5 major peaks is selected for each Aroclor. The RT window for each peak is determined from the initial calibration analysis. Identification of an Aroclor in the sample is based on pattern recognition in conjunction with the elution of 3-5 sample peaks within the RT windows of the corresponding peaks of the standard on both GC columns.

11.1.1.4 When an Aroclor is detected in a sample, a valid five-point calibration curve specific to that Aroclor must be run, followed by reanalysis of the sample or appropriately diluted sample with the detected Aroclor present. The Mean Calibration Factor (~~6~~5) will be used to quantitate the analyte in the sample.

11.1.1.5 The choice of the peaks used for Aroclor identification and the recognition of those peaks may be complicated by the environmental alteration of the Aroclors, and by the presence of coeluting analytes or matrix interferences, or both. Because of the alteration of test materials in the environment, Aroclors in samples may give patterns similar to, but not identical with, those of the standards.

11.1.1.6 If more than one Aroclor is observed in a sample, the Contractor must choose different peaks to quantitate each Aroclor. A peak common to both analytes present in the sample must not be used to quantitate either compound.

11.1.2 Gas Chromatograph/Mass Spectrometer (GC/MS) Confirmation of Aroclors

11.1.2.1 Any Aroclor analyte listed in Exhibit C (Aroclors) for which a concentration is reported from a GC/Electron Capture Detection (ECD) analysis must have the identification confirmed by GC/MS if the concentration is sufficient for that purpose. The following paragraphs are to be used as guidance in performing GC/MS confirmation, as appropriate. USEPA may require reanalysis of any affected samples at no additional cost to USEPA.

11.1.2.2 The GC/MS confirmation may be accomplished by one of three general means:

- Examination of the semivolatile GC/MS library search results [i.e., Tentatively Identified Compound (TIC) data]; or
- A second analysis of the semivolatile extract; or
- Analysis of the Aroclor extract, following any solvent exchange and concentration steps that may be necessary.

11.1.2.3 The semivolatile GC/MS analysis procedures outlined in Exhibit D (Analytical Methods for Semivolatiles) are based on the injection into the instrument of approximately 10 ng of a target compound in a 2 µL volume. The semivolatile Contract Required Quantitation Limit (CRQL) values in Exhibit C (Semivolatiles) are based on the sample concentration that corresponds to an on-column concentration (extract concentration) of 5 ng/µL of target analyte. Therefore, if an individual peak concentration for an Aroclor is greater than or equal to 5 ng/µL for both columns then GC/MS confirmation is required.

11.1.2.3.1 For water samples prepared according to the method in Section 10, the corresponding sample concentration is 500 µg/L.

11.1.2.3.2 For soil/sediment samples prepared according to the method described in Section 10, the corresponding sample concentration is 17,000 µg/kg.

11.1.2.3.3 Therefore, based on the values given above, any Aroclor sample in which a target analyte on-column concentration is greater than 5 ng/µL, should be confirmed by GC/MS analysis of the semivolatile extract.

11.1.2.4 In order to confirm the identification of the target Aroclor, the laboratory must also analyze a reference standard for the analyte. In order to demonstrate the ability of the GC/MS system to identify the analyte in question, the concentration of the standard should be 50 ng/µL for Aroclors.

11.1.2.5 The laboratory is advised that library search results from the NIST (1998 release or later) mass spectral library will not likely list the name of the Aroclor analyte as it appears in this analytical method, hence, the mass spectral interpretation specialist is advised to compare the Chemical Abstracts Service (CAS) Registry numbers for the Aroclors to those from the library search routine.

11.1.2.6 If the analyte cannot be confirmed from the semivolatile library search data for the original semivolatile GC/MS analysis, the laboratory may analyze another aliquot of the semivolatile sample extract after further concentration of the aliquot. This second aliquot must either be analyzed as part of a routine semivolatile GC/MS analysis, including instrument performance checks (DFTPP), or it must be analyzed along with separate reference standards for the analytes to be confirmed.

11.1.2.7 If the analyte cannot be confirmed by the procedure in Section 11.1.2.6, then an aliquot of the extract prepared for the GC/ECD analysis must be analyzed by GC/MS, following any necessary solvent exchange and concentration steps. As in Section 11.1.2.4, analysis of a reference standard is required if the GC/MS continuing calibration standard does not contain the analyte to be confirmed.

11.1.2.8 Regardless of which of the approaches above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the semivolatile extract, then the semivolatile method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the extract prepared for

the GC/ECD analysis, then the method blank extracted with the sample must be analyzed.

11.1.2.9 If the identification of the analyte cannot be confirmed by any of the GC/MS procedures above, and the concentration calculated from the GC/ECD analysis is greater than or equal to the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit (the value associated with the "U" qualifier) to a sample concentration equivalent to the concentration of the GC/MS reference standard, and qualify the results on Form I with one of the laboratory-defined qualifiers ("X", "Y", or "Z"). In this instance, define the qualifier explicitly in the Sample Delivery Group (SDG) Narrative, and describe the steps taken to confirm the analyte in the SDG Narrative.

11.1.2.10 For GC/MS confirmation of Aroclors, spectra of three characteristic peaks are required for both the sample component and the reference standard.

11.1.2.11 The purpose of the GC/MS analysis for the Aroclors is to confirm the presence of chlorinated biphenyls in Aroclors. The GC/MS analytical results for the Aroclors shall not be used for quantitation and the GC/MS results shall not be reported on Form I and Form X. The exception noted in Section 11.1.2.9 applies only to analytes that cannot be confirmed above the reference standard concentration.

11.2 Calculations

11.2.1 Aroclor Concentrations

11.2.1.1 Water

11.2.1.1.1 EQ. 7 Concentration Calculation for Water Samples

$$\text{Concentration } \mu g/L = \frac{(A_x)\,(V_t)\,(DF)\,(GPC)}{(\overline{CF})\,(V_o)\,(V_i)}$$

Where,

A_x = Area of the peak for the compound to be measured.

$\overline{CF}$ = Mean Calibration Factor from the specific five-point calibration.

V_o = Volume of water extracted in mL.

V_i = Volume of extract injected in µL. (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column).

V_t = Volume of the concentrated extract in µL. (If GPC is not performed, then V_t = 10000 µL. If GPC is performed, then V_t = 5000 µL).

DF = Dilution Factor. The DF for analysis of water samples by this method is defined as follows:

$$\frac{\text{µL most concentrated extract used to make dilution + µL clean solvent}}{\text{µL most concentrated extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

GPC = GPC factor. (If no GPC is performed, GPC = 1. If GPC is performed, then GPC = 2.0)

11.2.1.1.2 EQ. 8 On Column Concentration of Water Sample Extract

$$\text{On Column Concentration (ng/µL)} = \frac{(A_x)}{(\overline{CF})\,(V_i)}$$

Where,

A_x = Same as EQ. 7.

66 = Same as EQ. 7.

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column).

11.2.1.2 Soil/Sediment

11.2.1.2.1 EQ. 9 Concentration Calculation for Soil Samples

$$\text{Concentration µg/Kg (Dry weight basis)} = \frac{(A_x)\,(V_t)\,(DF)\,(GPC)}{(\overline{CF})\,(V_i)\,(W_s)\,(D)}$$

Where,

A_x, V_t, and **66** are as given for water, above.

V_i = Volume of extract injected in µL. (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column.)

$D = \frac{100 - \%\text{Moisture}}{100}$

W_s = Weight of sample extracted in g.

DF = Dilution Factor. The DF for analysis of soil/sediment samples by this method is defined as follows:

$$\frac{\text{µL most concentrated extract used to make dilution + µL clean solvent}}{\text{µL most concentrated extract used to make dilution}}$$

If no dilution is performed, DF = 1.0

GPC = GPC factor = 2

11.2.1.2.2 EQ. 10 On Column Concentration of Soil Sample Extract

$$\text{On Column Concentration (ng/µL)} = \frac{(A_x)}{(\overline{CF})\,(V_i)}$$

Where,

A_x = Same as EQ. 7.

CF = Same as EQ. 7.

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column).

11.2.2 Target Compounds

The quantitation of Aroclors must be accomplished by comparing the heights or the areas of each of the 3-5 major peaks of the Aroclor in the sample with the **CF** for the same peaks established during the specific five-point calibration. The concentration of multi-component analytes is calculated by using Equations 7 and 9, where A_x is the area for each of the major peaks of the Aroclor. The concentration of each peak is determined and then a mean concentration for the 3-5 major peaks is determined on each column.

11.2.2.1 Note that the **CF**s used for the quantitation of Aroclors are the **CF**s from the concentration of the specific five-point calibration.

11.2.2.2 The higher <u>mean</u> concentration (from 3-5 peaks) is reported on Form I, and the two mean concentrations reported on Form X. The two mean concentrations are compared by calculating the Percent Difference (%Difference) using Equation 11.

EQ. 11 Percent Difference Calculation

$$\%\text{Difference} = \frac{\text{Conc}_H - \text{Conc}_L}{\text{Conc}_L} \times 100$$

Where,

$Conc_H$ = The higher of the two concentrations for the target compound in question.

$Conc_L$ = The lower of the two concentrations for the target compound in question.

NOTE: Using this equation will result in Percent Difference values that are always positive.

11.2.3 CRQL Calculation

11.2.3.1 Water Samples

EQ. 12 Adjusted CRQL Calculation for Water Samples

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(V_x)(V_t)(V_y)(DF)}{(V_o)(V_c)(V_i)}$$

Where,

V_t, DF, V_o, and V_i = As given in Equation 7.

V_x = Contract sample volume (1000 mL).

V_y = Contract injection volume (1 µL or 2 µL).

V_c = Contract concentrated extract volume (10,000 µL if GPC was not performed and 5,000 µL if GPC was performed).

11.2.3.2 Soil/Sediment Samples

EQ. 13 Adjusted CRQL Calculation for Soil/Sediment Samples

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(W_x)(V_t)(V_y)(DF)}{(W_s)(V_c)(V_i)(D)}$$

Where,

V_t, DF, W_s, V_i, and D = As given in Equation 9.

W_x = Contract sample weight (30 g).

V_y = Contract injection volume (1 µL or 2 µL).

V_c = Contract concentrated extract volume (10,000 µL if GPC was not performed).

11.2.4 Surrogate Recoveries

The concentrations for surrogate compounds can be calculated by using Equation 7 and substituting the CF from the most recent initial calibration for the 66.

11.2.4.1 Calculate surrogate recoveries for each GC column using Equation 14.

EQ. 14 Surrogate Recovery Calculation

$$\text{Percent Recovery} = \frac{Q_d}{Q_a} \times 100$$

Where,

Q_d = Quantity determined by analysis.

Q_a = Quantity added.

11.2.4.2 The advisory limits for the recovery of the surrogates are 30-150% for both surrogate compounds.

11.2.4.3 As these limits are only advisory, no further action is required by the laboratory; however, frequent failure to meet the limits for surrogate recovery warrants investigation by the laboratory, and may result in questions from USEPA.

11.2.4.4 Surrogate recovery data from both GC columns are reported (see Exhibit B).

11.3 Technical Acceptance Criteria for Sample Analysis

The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

11.3.1 Samples must be analyzed under the GC/ECD operating conditions in Section 9. The instrument must have met all initial calibration, calibration verification, and blank technical acceptance criteria. Sample data must be bracketed at 12-hour intervals (or less) by acceptable analyses of calibration verification standards described in Section 10.3.2.1.

11.3.2 The samples must be extracted and analyzed within the contract required holding times.

11.3.3 The samples must have an associated method blank meeting the technical acceptance criteria for method blanks.

11.3.4 The RT for each of the surrogates must be within the RT window (Section 9.2.4.3) for both GC columns.

11.3.5 No target analyte concentrations may exceed the upper limit of the initial calibration or else the extract must be diluted and reanalyzed.

11.3.6 If a valid initial calibration is not available, then a five-point calibration curve specific for any identified Aroclor must be analyzed during a valid analytical sequence on the same instrument and column upon its detection in a sample. Reanalysis of the sample or required diluted sample with the detected Aroclor is necessary and billable to USEPA.

11.3.7 The identification of Aroclors is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for Aroclors.

11.3.7.1 A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3-5 peaks should include at least one peak that is unique to that Aroclor.

11.3.7.2 Chromatograms must display the largest peak of any Aroclor detected in the sample at less than full scale.

11.3.7.3 If an extract must be diluted, chromatograms must display the peaks chosen for quantitation of Aroclors between 25 and 100% of full scale.

11.3.7.4 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.3.7.5 If the chromatogram of any sample needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample analysis technical acceptance criteria MUST be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank will require reextraction and reanalysis at no additional cost to USEPA. Any samples analyzed that do not meet the technical acceptance criteria will require reextraction and/or reanalysis at no additional cost to USEPA.

11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be reanalyzed at no additional cost to USEPA after the corrective action.

11.4.3 The extract from samples that were cleaned up by GPC using an automated injection system, and have surrogate recoveries outside the lower advisory surrogate acceptance limits, must be checked to assure that the proper amount was injected on the GPC column. If insufficient volume was injected, the sample must be reprepared and reanalyzed at no additional cost to USEPA.

11.4.4 If sample chromatograms have a high baseline or interfering peaks, inspect the system to determine the cause of the problem (e.g., carryover, column bleed, dirty ECD, contaminated gases, leaking septum, etc.). After correcting the problem, reanalyze the sample

extracts. If the problem with the samples still exists, then those samples must be reextracted and reanalyzed. Samples that cannot be made to meet the given specifications after one reextraction and cleanup procedures (sulfuric acid and GPC cleanups) are reported in the SDG Narrative and do not require further analysis.

12.0 QUALITY CONTROL (QC)

12.1 Method Blanks

12.1.1 Summary of Method Blanks

A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified sodium sulfate for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2 Frequency of Method Blanks

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spikes/Matrix Spike Duplicates (MS/MSDs) and Performance Evaluation (PE) samples]. In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples.
- Be analyzed on each Gas Chromatograph/Electron Capture Detector (GC/ECD) system used to analyze associated samples.

12.1.3 Procedure for Method Blank Preparation

12.1.3.1 For Aroclor analyses, a method blank for water samples consists of a 1 L volume of reagent water spiked with 1.0 mL of the surrogate spiking solution (Section 7.2.4.1). For soil/sediment samples, the method blank consists of 30 g of sodium sulfate spiked with 1 mL of the surrogate spiking solution.

12.1.3.2 Extract, concentrate, and analyze method blanks according to Section 10.

12.1.3.3 Calculate method blank results according to Section 11.

12.1.4 Technical Acceptance Criteria for Method Blanks

12.1.4.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on both GC columns.

12.1.4.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2, using the procedure above and in Section 10 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria. If samples are cleaned up by Gel Permeation Chromatography (GPC), then associated method blanks must undergo GPC cleanup. All GPC cleanup must be performed on an instrument meeting the technical acceptance criteria for GPC calibration checks. A method blank

must be analyzed within a valid 12-hour sequence, as described in Section 10.3.2.1.

12.1.4.3 The concentration of the target compounds [Exhibit C (Aroclors)] in the method blank must be less than the Contract Required Quantitation Limit (CRQL) for each target compound.

12.1.4.4 The method blank must meet all sample technical acceptance criteria in Sections 11.3.4 - 11.3.7.

12.1.4.5 Surrogate recoveries must fall within the acceptance windows of 30-150%. In the case of the method blank(s), these limits are not advisory.

12.1.2.5 Corrective Action for Method Blanks

12.1.2.5.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the system to be out-of-control.

12.1.2.5.2 If contamination is a problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and sample processing hardware that lead to discrete artifacts and/or elevated baselines be investigated and appropriate corrective actions be taken and documented before further sample analysis. All samples associated with a contaminated method blank must be reextracted/reanalyzed at no additional cost to USEPA.

12.1.2.5.3 If the surrogate recoveries in the method blank do not meet the acceptance criteria listed in Section 12.1.4.5, first reanalyze the method blank. If surrogate recoveries do not meet the acceptance criteria after reanalysis, the method blank and all samples associated with that method blank must be reextracted and reanalyzed at no additional cost to USEPA.

12.1.2.5.4 If the method blank failed to meet the criteria listed in Sections 12.1.4.2 and 12.1.4.4, the problem must be corrected and the method blank must be reanalyzed.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for Aroclor analyses, USEPA has prescribed a mixture of Aroclor target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD Analysis

12.2.2.1 An MS/MSD must be extracted and analyzed for every 20 field samples of a similar matrix in a Sample Delivery Group (SDG). MS/MSD samples shall be analyzed unless otherwise specified on the Traffic Report/Chain of Custody Record. If no MS/MSD samples are specified on the Traffic Report/Chain of Custody (TR/COC) Record, the Contractor shall contact the Sample Management Office (SMO) to confirm that MS/MSD analyses are not required.

12.2.2.2 As part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field blanks may be delivered to a laboratory for analysis. Do not perform MS/MSD analysis on a water rinsate sample or field blank.

12.2.2.3 If a USEPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of another sample other than the one designated by USEPA shall be documented in the SDG Narrative.

12.2.2.4 If there is insufficient sample volume remaining in any of the samples in an SDG to perform an MS/MSD, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than required by the contract, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

12.2.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD when the Region did not designate samples to be used for this purpose. If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 Water Samples

For water samples, measure out two additional 1 L aliquots of the sample chosen for spiking. Adjust the pH of the samples to between 5 and 9 with low sodium hydroxide or concentrated sulfuric acid (if required) and fortify each with 1 mL of matrix spiking solution (Section 7.2.4.2). Using a syringe or volumetric pipet, add 1 mL of surrogate spiking solution to each sample (Section 7.2.4.1). Extract, concentrate, cleanup, and analyze the MS/MSDs according to Section 10.0.

12.2.3.2 Soil/Sediment Samples

For soil/sediment samples, weigh out two additional 30 g (to the nearest 0.1 g) aliquots of the sample chosen for spiking. Add 1 mL of matrix spiking solution (Section 7.2.4.2) and 1 mL of

surrogate solution (Section 7.2.4.1). Extract, concentrate, cleanup, and analyze the MS/MSDs according to Section 10.0.

12.2.3.2 Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do not further dilute MS/MSD samples to get either spiked or nonspiked analytes within calibration range.

12.2.4 Calculations for MS/MSD

12.2.4.1 The Percent Recoveries (%Rs) and the Relative Percent Difference (RPD) between the recoveries of each of the compounds in the Matrix Spike samples will be calculated and reported by using the following equations:

EQ. 15 Percent Recovery of Spike Compounds in MS/MSD Samples

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample Result.

SR = Original Sample Result.

SA = Spike Added.

EQ. 16 Relative Percent Difference Between MS/MSD Spike Recoveries

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

RPD = Relative Percent Difference.

MSR = Matrix Spike recovery.

MSDR = Matrix Spike Duplicate recovery.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 The requirements below apply independently to <u>each</u> GC column and to all instruments used for these analyses. Quantitation must be performed on both GC columns.

12.2.5.2 All MS/MSDs must be prepared and analyzed at the frequency described in Section 12.2.2 using the procedure above, and in Section 10, on a GC/ECD system meeting the initial calibration, calibration verification, and blank technical acceptance criteria. MS/MSDs must be cleaned up when required. MS/MSDs must be bracketed at 12-hour intervals (or less) by acceptable calibration verification described in Section 10.3.2.1.

12.2.5.3 The samples must be extracted and analyzed within the contract required holding times.

12.2.5.4 The Retention Time (RT) for each of the surrogates must be within the RT window as calculated in Section 9 for both GC columns.

12.2.5.5 The limits for Matrix Spike compound recovery and RPD are given in Table 1. As these limits are only advisory, no further action by the laboratory is required. However, frequent failure to meet the limits for recovery or RPD warrants investigation by the laboratory, and may result in questions from USEPA.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD that fails to meet the technical acceptance criteria for MS/MSD must be reanalyzed at no additional cost to USEPA.

12.3 Laboratory Control Sample (LCS)

12.3.1 Summary of LCS

The LCS is an internal laboratory QC sample designed to assess (on an SDG-by-SDG basis) the capability of the contractor to perform the analytical method listed in this Exhibit.

12.3.2 Frequency of LCS

The LCS must be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix per SDG. The LCS must be extracted and analyzed concurrently with the samples in the SDG using the same extraction protocol and instrumentation as the samples in the SDG.

12.3.3 Procedure for Preparing LCS

12.3.3.1 Water Samples

For water samples, measure out two additional 1 L aliquots of the reagent water and spike with 1.0 mL of the LCS spiking solution (Section 7.2.4.3) and 1.0 mL of the surrogate spiking solution (Section 7.2.4.1). Extract, concentrate, and analyze the sample according to Section 10.

12.3.3.2 Soil/Sediment Samples

For soil samples, measure out two additional 30 g of a clean reference matrix (e.g., sodium sulfate) and spike with 1.0 mL of the LCS spiking solution (Section 7.2.4.3) and 1.0 mL of surrogate spiking solution (Section 7.2.4.1). Extract, concentrate, and analyze the LCS according to Section 10.

12.3.4 Calculations for LCS

12.3.4.1 Calculate the results according to Section 11.

12.3.4.2 Calculate individual compound recoveries of the LCS using Equation 14.

12.3.5 Technical Acceptance Criteria for LCS

12.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.3.5.2 The LCS must be analyzed at the frequency described in Section 12.3.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.3.5.3 The LCS must be prepared as described in Section 12.3.3.

12.3.5.4 The LCS must meet all sample technical acceptance criteria in Section 11.3.

12.3.5.5 The Percent Recovery (%R) for each of the compounds in the LCS must be within the recovery limits listed in Table 2.

12.3.6 Corrective Action for LCS

12.3.6.1 If the LCS technical acceptance criteria for the surrogates or the LCS compound recovery are not met, check calculations, the surrogate and LCS solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and LCS recovery criteria.

12.3.6.2 LCS technical acceptance criteria MUST be met before data are reported. LCS contamination from laboratory sources or any LCS analyzed not meeting the technical acceptance criteria will require reextraction and reanalysis of the LCS at no additional cost to USEPA.

12.3.6.3 All samples (including MS/MSDs and PE samples) and required blanks, prepared and analyzed in an SDG with an LCS that does not meet the technical acceptance criteria, will also require reextraction and reanalysis at no additional cost to USEPA.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasiblely reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Polychlorinated Biphenyls (PCBs) by Gas Chromatography. SW-846 Method 8082, Revision 0. December 1996.

16.2 US Environmental Protection Agency. Separatory Funnel Liquid-Liquid Extraction. SW-846 Method 3510C, Revision 3. December 1996.

16.3 US Environmental Protection Agency. Continuous Liquid-Liquid Extraction. SW-846 Method 3520C, Revision 3. December 1996.

16.4 US Environmental Protection Agency. Automated Soxhlet Extraction. SW-846 Method 3541, Revision 0. September 1994.

16.5 US Environmental Protection Agency. Pressurized Fluid Extraction (PFE). SW-846 Method 3545, Revision 0. December 1996.

16.6 US Environmental Protection Agency. Ultrasonic Extraction. SW-846 Method 3550B, Revision 2. December 1996.

16.7 US Environmental Protection Agency. Sulfuric Acid/Permanganate Cleanup. SW-846 Method 3665A, Revision 1. December 1996.

16.8 US Environmental Protection Agency. Gel-Permeation Cleanup. SW-846 Method 3640A, Revision 1. September 1994.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Matrix Spike Recovery and Relative Percent Difference Limits

Compound	Percent Recovery QC Limits	RPD
AR1016	29-135	15
AR1260	29-135	20

Table 2

Laboratory Control Sample Recovery - Water and Soil

Compound	Percent Recovery QC Limits
AR1016	50-120
AR1260	50-150